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(54) [Title of the Invention] Copper Alloy for Electronic Materials of Superior Surface Properties and Method for Its Production

(57) [Abstract]

[Problem] To provide a copper alloy for electronic materials having excellent solderability and plating properties and of superior stress relaxation characteristics in a Cu-Ni-Si alloy having sufficient strength and electric conductivity.

[Means for Solving Problem] A copper alloy for electronic materials of superior strength, electric conductivity and surface characteristics that contains 1.5 to 4.0 mass percent (hereafter indicated as %) Ni, 0.30 to 1.2% Si and 0.05 to 0.20% Mg, that is prepared so that it has weight ratios of $\text{Ni/Si} = 3\text{--}7$ and $\text{Si/Mg} \leq 8.0$, in which the balance is Cu and unavoidable impurities, in which the ratio of the Mg peak intensity/the Si peak intensity of the Auger electron spectrum in the outermost surface of the material after the final treatment is greater than 1.0.

[Claims]

[Claim 1] A copper alloy for electronic materials of superior strength, electric conductivity and surface characteristics that contains 1.5 to 4.0 mass percent (hereafter indicated as %) of Ni, 0.30 to 1.2% Si and 0.05 to 0.20% Mg, that is prepared so that it has weight ratios $\text{Ni/Si} = 3\text{-}7$ and $\text{Si/Mg} \leq 8.0$, in which the balance is Cu and unavoidable impurities, in which the ratio of the Mg peak intensity to the Si peak intensity of the Auger electron spectrum in the outermost surface of the material after the final treatment is greater than 1.0.

[Claim 2] A copper alloy for electronic materials of superior strength, electric conductivity and surface characteristics characterized in that it contains 1.5 to 4.0% Ni, 0.30 to 1.2% Si and 0.05 to 0.20% Mg, that it contains a total amount of 0.005 to 2.0% of one or more of the following elements: Zn, Sn, Fe, Ti, Zr, Cr, Al, P, Mn, Ag or Be, that is prepared so that it has weight ratios of $\text{Ni/Si} = 3\text{-}7$ and $\text{Si/Mg} \leq 8.0$, that the balance is Cu and unavoidable impurities, and that the ratio of the Mg peak intensity to the Si peak intensity of the Auger electron spectrum in the outermost surface of the material after the final treatment is greater than 1.0.

[Claim 3] A method for the production of a copper alloy for electronic materials as described in the claim 1 or 2, characterized in that the final heat treatment is performed at a material temperature of 300 to 600°C in a reducing gas or inert gas atmosphere.

[Detailed Description of the Invention]

[0001]

[Technological field of the invention] This invention relates to a copper alloy for electronic materials of superior strength, electric conductivity and stress relaxation characteristics and excellent surface characteristics, that is, excellent solderability and plating properties.

[0002]

[Prior art] Copper alloys for electronic materials that are used in lead frames, terminals and connectors must endow products with the basic characteristics of high strength and high electric conductivity or heat transfer capacity. In addition, it has become necessary in recent years to make the materials thinner because of the requirements for making electronic components smaller and with a higher level of integration. For lead frames, terminals and connectors, there have been increases in the number of leads and a reduction of pitch. Further, because of increased complexity of shape and increased demands for reliability in assembly and mounting, the materials that are used should have excellent solderability and plating properties in addition to being of superior mechanical strength and electric conductivity. Excellent stress relaxation properties are also required for terminals and connector components from the standpoint of long-term reliability.

[0003] In recent years, from the standpoint of high strength and high electric conductivity, there has been an increase in the amount of age-hardening copper alloy used as copper alloy for electronic materials in place of copper alloys strengthened by said solid solution of which bronze and brass are

representative. By age-hardening supersaturated solid solutions in which age-hardening copper alloys have been put into solid solution, minute deposits can be uniformly dispersed, the strength of the alloy can be increased, and, at the same time, the amounts of elements in solid solution in the copper can be decreased and electric conductivity is increased.

[0004] Consequently, they have superior mechanical properties such as spring properties and can be used as materials of excellent electric conductivity and heat transfer properties. Here, many reactive elements can be employed as deposited elements. Further, there are instances in which reactive metals can also be added for the purpose of improving the properties of alloys. Of the age-hardening copper alloys, Cu-Ni-Si alloy is a representative copper alloy having both high strength and high electric conductivity and has been put into practical use as a material for electronic devices. This copper alloy has the characteristic that its strength and electric conductivity are increased by the fact that that fine Ni-Si intermetallic compound particles are deposited in the copper matrix.

[0005]

[Problems the invention is intended to solve] Because Cu-Ni-Si alloys contain Si, which is a reactive metal, in the manufacturing process, heat treatments are performed in a reducing gas or inert gas atmosphere. However, when heat treatment is performed in such a gas atmosphere, the Si reacts with oxygen, producing a film of SiO_2 on the surface layer, even in a good atmosphere in which the oxygen concentration in the heating furnace is less than 10 ppm. When a film of SiO_2 is present in the surface layer of the material, this is

the cause of marked deterioration in solderability and plating properties, for which reason it is necessary to remove the oxide film before soldering and plating.

However, because SiO_2 is insoluble in acids, the film cannot be easily removed.

Consequently, the surface of the material must be ground before the heat treatment, with productivity being thus markedly decreased.

[0006] This invention was developed in order to solve the problems described above and its object is to provide a copper alloy for electronic materials that has excellent solderability and plating properties and that is of superior stress relaxation properties in a Cu-Ni-Si alloy having sufficient strength and electric conductivity.

[0007]

[Means for solving the problems] When the inventors conducted repeated research on Cu-Ni-Si alloys in order to solve the problems described above, they discovered that excellent materials as such copper alloys for electronic materials can be provided by adjusting the components of Cu-Ni-Si alloys by adding Mg to them, and, as required, by having them also contain Zn, Sn, Fe, Ti, Zr, Cr, Al, P, Mn, Ag and Be.

[0008] Specifically, the specific subjects of this invention are: (1) a copper alloy for electronic materials of superior strength, electric conductivity and surface characteristics, characterized in that that contains 1.5 to 4.0 mass percent (hereafter indicated as %) Ni, 0.30 to 1.2% Si and 0.05 to 0.20% Mg, that is prepared so that it has weight ratios of $\text{Ni/Si} = 3\text{-}7$ and $\text{Si/Mg} \leq 8.0$, in which the balance is Cu and unavoidable impurities, in which the ratio of the Mg peak

intensity to the Si peak intensity of the Auger electron spectrum in the outermost surface of the material after the final treatment is greater than 1.0.

[0009] (2) A copper alloy for electronic materials of superior strength, electric conductivity and surface characteristics, characterized in that it contains 1.5 to 4.0% Ni, 0.30 to 1.2% Si and 0.05 to 0.20% Mg, that it contains a total amount of 0.005 to 2.0% of one or more of the following elements: Zn, Sn, Fe, Ti, Zr, Cr, Al, P, Mn, Ag or Be, that is prepared so that it has weight ratios of Ni/Si = 3-7 and $\text{Si/Mg} \leq 8.0$, that the balance is Cu and unavoidable impurities and that the ratio of the Mg peak intensity to the Si peak intensity of the Auger electron spectrum in the outermost surface of the material after the final treatment is greater than 1.0.

[0010] (3) A method for the production of a copper alloy for electronic materials as described in (1) or (2), characterized in that the final heat treatment is performed at a material temperature of 300 to 600°C in a reducing gas or inert gas atmosphere.

[0011]

[Embodiments of the invention] Next, we shall explain the reasons that, in this invention, the composition range of the copper alloy, the Ni/Si and Si/Mg concentration ratios and the Auger electron peak intensity ratios of Mg and Si on the topmost surface of the materials after the final heat treatment are limited as described above and their actions.

[0012] (1) Ni and Si

Ni and Si form mutual and fine deposited particles of Ni and Si intermetallic compounds in which Ni_2Si is the principal compound as the result of performing aging-hardening treatment, with the strength of the alloy being markedly increased, on the one hand, and with electric conductivity also being maintained at a high level. However, when the Ni content is less than 1.5% or the Si content is less than 0.30%, the desired strength is not obtained even if other components are added. Further, when the Ni content exceeds 4.0% or the Si content exceeds 1.2%, even though sufficient strength is obtained, the electric conductivity that is desired is decreased. In addition, coarse Ni-Si particles (crystallized substances and deposited substances) that do not contribute to the improvement of strength are produced in the matrix phase and decreases are brought about in bending processability, etching capacity and plating properties. Therefore, the content of Ni was set at 1.5 to 4.0% and the content of Si was set at 0.30 to 1.2%.

[0013] (2) Mg

Mg has the effect of bringing about great improvement in stress relaxation characteristics and has the effect of improving hot rolling characteristics. However, when it is present in an amount of less than 0.05%, these effects are not obtained. When it is present in an amount greater than 0.20%, casting characteristics (decrease in cast texture quality), hot rolling characteristics and resistance to heat peeling of the plating are decreased. For this reason, Mg content was set at 0.05 to 0.20%.

[0014] (3) Ni/Si and Si/Mg weight ratios

The reason for stipulating the weight ratio of Si content and Ni content (written as Ni/Si) as 3 to 7 was to further increase electric conductivity after aging treatment by bringing the weight ratio of Ni and Si in the alloy closer to the concentration ratio of the Ni and Si of Ni_2Si , which is the intermetallic compound. When Ni/Si is less than 3, the Si concentration is excessive relative to the Ni_2Si composition, for which reason, in addition to electric conductivity being decreased, a formation of an Si oxide film on the surface of the material during heat treatment is facilitated due to the fact that the amount of Si in solid solution is increased in the matrix. This is a cause of deterioration of solderability and plating properties.

[0015] The weight ratio relative to the Ni_2Si composition is $\text{Ni/Si} = 4$. In order to bring about a decrease in the amount of Si in solid solution for the reason described above, the amount of Ni relative to the Ni_2Si composition should be somewhat in excess. However, when Ni/Si exceeds 7, the amount of excess Ni relative to the Ni_2Si composition is greatly increased, for which reason the desired electric conductivity cannot be obtained. Consequently, the weight ratio of Si and Ni for the purpose of obtaining excellent electric conductivity, solderability and plating properties should be $\text{Ni/Si} = 3$ to 7, and, more preferably, 4.5.

[0016] The reason for stipulating the weight ratio of Mg content and Si content (described hereafter as Si/Mg) as 8.0 or less was to make the composition of the oxide that is formed on the surface of the material during the final heat treatment a composition rich in Mg oxide relative to the content of Si

oxide. Much of the Si that is contained in the alloy of this invention forms compounds with Ni. However, some of the Si goes into solid solution in the matrix and the Si oxide SiO_2 is produced in the surface layer of the material during the heat treatment. Further, because Mg is also a reactive metal, the Mg oxide MgO is produced during the heat treatment. These oxides, in correspondence to their volumes of production, are 2MgOSiO_2 and MgOSiO_2 compounds.

[0017] Of the oxides described above, MgO and 2MgOSiO_2 which are produced in the MgO-rich region are soluble in acids while SiO_2 and MgOSiO_2 which are produced in the SiO_2 rich region are insoluble in acids (are not acted upon by acids). When the composition of the surface oxide after the heat treatment is in the MgO-rich region, the surface oxide layer can easily be removed by washing with acid before mounting, for which reason solderability and plating properties are excellent. It was ascertained that setting $\text{Ni/Si} = 3$ to 7 and $\text{Si/Mg} \leq 8.0$ is effective for making the oxide composition after heat treatment in the component composition of the alloy of this invention into an MgO-rich surface layer. Consequently, a weight ratio of Mg and Si of 8.0 or less, and, preferably, of 6.0 or less, in the component composition of the alloy of this invention is effective for obtaining excellent solderability and excellent plating properties.

[0018] (4) The Auger electron peak intensity ratio

In addition to stipulating the component ranges of Ni, Si and Mg as described above, further stipulating the Ni/Si ratio and the Si/Mg ratio is effective

for obtaining copper alloys of superior surface properties. However, there are cases in which the composition of the surface oxide layer does not become an Mg oxide-rich region depending on the manufacturing conditions. It is thought that this is due to the composite action of the added components and the amounts of these components and heat treatment conditions (heating temperature and time). Accordingly, the inventors conducted detailed studies, and, as the result, it was ascertained the desired alloys can be obtained by regulation of the components and regulating the heat treatment conditions so that the Mg peak intensity/Si peak intensity ratio of the Auger electron spectrum of the topmost surface of the material after the final heat treatment is greater than 1.0.

[0019] Specifically, the intensity (peak amplitude) ratio of the Mg subpeak (energy value: 1170 to 1190 eV) and of the Si subpeak (energy value: 1605 to 1625 eV) in the differential spectrum obtained by qualitative analysis with Auger electron spectroscopy should be 1.0 or greater. The reason for making evaluations based on subpeaks is that, although a main peak is present on the low energy side for both Mg and Si, the two energy values are close to each other and the peaks of the other elements are also concentrated in similar positions, for which reason the peaks are superimposed on each other and identification is difficult. Consequently, in order to obtain excellent solderability and excellent plating properties, in addition to stipulating the Ni/Si and Si/Mg ratios in the component composition of the alloy of this invention, the Mg peak intensity/Si peak intensity ratio of the Auger electron spectrum of the topmost

surface of the material after the heat treatment should be greater than 1.0, and, preferably, greater than 1.5.

[0020] (5) Zn, Sn, Fe, Ti, Zr, Cr, Al, P, Mn, Ag or Be

Zn, Sn, Fe, Ti, Zr, Cr, Al, P, Mn, Ag or Be have the action of improving the strength and heat resistance of Cu-Ni-Si alloys. Of them, Zn has the effect of improving the heat resistance of solder connections and Fe has the effect of making texture finer. Further, Ti, Zr, Al and Mn have the effect of improving hot rolling characteristics. The reason for this is that these elements have a strong affinity for yellow sulfur, for which reason they form compounds with yellow sulfur and decrease the segregation of yellow sulfur at the ingot grain boundaries, the cause of cracking during hot rolling. When the the total content of Zn, Sn, Fe, Ti, Zr, Cr, Al, P, Mn, Ag or Be is less than 0.005%, the effects described above are not obtained. On the other hand, when their total content exceeds 2.0%, electric conductivity is markedly decreased. Accordingly, their total content is set at 0.005 to 2.0%.

[0021] Next, we shall describe the method of production for obtaining this alloy. The alloy of this invention is produced by repeated rolling and heat treatment. In the production process of ordinary copper alloy, there are many instances in which a heat treatment is performed after the final cold rolling. The objectives of this heat treatment differ depending on processing history and the intended use of the product. However, they can generally be classified into stress-relieving annealing, aging treatment and temper annealing. It is desirable that these heat treatments be performed in a reducing gas or inert gas

atmosphere. However, it is difficult to obtain the target characteristics at material temperatures of less than 300°C. That is, prolonged annealing must be performed in order to obtain the target characteristics and this is not economical. When 600°C is exceeded, surface oxidation is markedly promoted even with heat treatment in a reducing atmosphere. Moreover, because deposited particles in the matrix phase go into solid solution, the strength and electric conductivity are decreased. In addition, there is marked promotion of surface oxidation regardless of the temperature range when heat treatments are conducted in air. When the material temperature exceeds 600°C in heat treatment in air, the surface oxide film cannot be completely removed simply by washing with acid even when certain amounts and weight ratios of Ni, Si, and Mg are stipulated. For this reason, grinding of the corresponding film on the material surface is necessary. Consequently, it is necessary that the final heat treatment of the alloy in this invention be performed in a reducing gas or inert gas atmosphere and in a range of material temperatures of 300 to 600°C.

[0022]

[Working examples] We shall now describe this invention on the basis of working examples. Copper alloys comprised of the various components shown in Table 1 were melted in a high frequency melting furnace and were cast into ingots of 20 mm in thickness.

[0023]

[Table 1]

Alloys of This Invention and Comparison Examples

	No.	Components (wt%)				Weight ratios		Material temperature in final annealing (°C)
		Ni	Si	Mg	Secondary component	Ni/Si	Si/Mg	
Alloys of this invention	1	2.60	0.65	0.09	-	4.0	7.2	450
	2	2.73	0.82	0.12	-	3.3	6.8	450
	3	3.20	0.57	0.19	-	5.6	3.0	500
	4	2.75	0.41	0.06	-	6.7	6.8	550
	5	1.63	0.35	0.06	0.42Fe	4.7	5.8	550
	6	2.54	0.66	0.18	0.11Zn 0.28Sn	3.8	3.7	600
	7	2.11	0.52	0.06	0.01Ti 0.03Cr	4.1	6.5	450
	8	1.82	0.44	0.07	0.15Al	4.1	6.3	500
	9	2.77	0.71	0.16	0.06P 0.41Zn	3.9	4.4	300
	10	2.20	0.40	0.11	0.007Be	4.5	4.5	350
	11	3.36	0.58	0.08	0.31Zr	5.8	7.3	450
	12	2.64	0.60	0.15	0.03Ag 0.08*Mn	4.4	4.0	500
Comparison alloys	1	1.22	0.35	0.08	-	4.9	3.1	500
	2	3.90	1.28	0.19	-	3.0	6.7	500
	3	2.02	0.31	0.04	-	6.5	7.8	500
	4	2.15	0.55	0.24	-	3.9	2.5	500
	5	2.61	0.68	0.18	0.78Al 1.43Sn	4.5	3.2	500
	6	2.85	0.38	0.14	-	7.5	2.7	500
	7	1.64	0.79	0.17	-	2.1	4.6	500
	8	2.75	0.88	0.10	-	3.1	8.8	500
	9	2.80	0.68	0.05	0.52Fe	4.1	13.6	500
	10	1.90	0.45	0.01	1.12Zn 0.12Sn	4.2	45	500
	11	2.60	0.65	0.09	-	4.0	7.2	650
	12	2.60	0.65	0.09	-	4.0	7.2	280

*somewhat illegible—possibly 0.03—Trans. note.

[0024] Next, these ingots were hot rolled to a thickness of 8 mm and surface planing was performed to remove the scale on the surface, after which they were made into plates of 1 mm thickness by cold rolling. Following this, solution treatment was performed at a temperature of 850°C, after which they were cold rolled to 0.4 mm. Aging treatment of each of the compositions was then performed for 5 hours at temperatures of 400 to 600°C at which maximum

strength can be obtained, after which, so that high strength could be obtained, they were made into plates of 0.25 mm thickness by cold rolling, and, finally, they were subjected to appropriate heat treatment for 10 seconds to 5 minutes at the temperatures shown in Table 1 in a reducing gas (75% H_2 -25% N_2) atmosphere.

[0025]

Auger analysis of the test materials after the final heat treatment was performed by means of a scanning micro-Auger electron spectroscopic analyzer, with qualitative analyses of three tubes being performed at an electron gun acceleration voltage of 5 kV and in an analysis domain of $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$. The intensity ratios (amplitude ratios) of the Mg subpeak and the Si subpeak on the spectrum of the differential side were determined and averages were found and taken as the Auger peak intensity ratios.

[0026] Evaluations of the characteristics of the various alloys that were obtained in this way were made. The results are shown in Table 2.

[0027]

[Table 2]

	No.	Subpeak intensity ratio Mg/Si	Tensile strength N/mm ²	Electric conduction rate %IACS	Stress relaxation rate %	Solder wetting time seconds
Alloys of this invention	1	1.4	710	50	18	1.0
	2	2.3	721	44	16	0.8
	3	4.7	698	45	15	0.6
	4	1.1	684	47	19	1.4
	5	2.6	612	54	20	1.2
	6	3.9	654	49	15	0.9
	7	1.3	678	52	17	1.1
	8	1.8	647	55	20	0.9
	9	1.5	702	41	20	1.5
	10	2.2	725	52	17	1.2
	11	1.6	714	41	19	1.0
	12	5.1	712	48	19	0.8
Comparison alloys	1	1.4	483	56	19	0.8
	2	2.5	724	37	17	1.1
	3	1.1	627	48	26	1.5
	4	4.8	698	49	16	0.9
	5	2.1	690	30	17	1.4
	6	1.9	710	36	18	1.3
	7	0.9	621	38	17	2.2
	8	0.8	703	47	20	2.4
	9	0.7	685	44	19	3.4
	10	0.3	644	45	29	× solder not cast
	11	0.6	502	47	15	2.6
	12	0.8	694	49	17	2.3

[0028] For strength, determinations were made of tensile strength with a tensile testing machine. Electric conductivity was evaluated by the electric conduction rate (%IACS). Stress relaxation characteristics were found by evaluating the stress relaxation rate in air at 150°C after 1000 hours of loading by loading 80% bending stress of 0.2% yield strength. Surface characteristics were evaluated by solderability. The evaluation of solderability was performed by the meniscograph method in which the test strip was immersed for 10 seconds at a depth of 2 mm in a 60% Sn-Pb bath at $235 \pm 3^\circ\text{C}$ and the time up to complete wetting of the solder and solder wetting time were measured. The pretreatment before the solderability evaluation was degreasing with acetone, after which the

test strip was immersed for 10 seconds in a 10 vol% aqueous solution of sulfuric acid and stirred as an acid wash and then washed with water and dried, after which the test strip was immersed for 5 seconds in a 25% rosin-ethanol solution and cefurax was applied. A solder wetting time of less than 2.0 seconds is generally preferred.

[0029] As can be seen from Table 2, the alloys of this invention Nos. 1 to 12 exhibited superior strength, electric conductivity, stress relaxation characteristics and solderability. There were particular good stress relaxation rates of 20% or less for all alloys of this invention and there were good solder wetting times of 1.5 seconds or less.

[0030] On the other hand, of the comparison alloys, Nos. 1 to 5 are partially different in composition from the alloys of this invention. When compared to the alloys of this invention, No. 1 is of poorer strength because of the low Ni content. No. 2 has a poor electric conduction rate because of its high Si content. No. 3 has poor stress relaxation characteristics because of its low Mg content. No. 4 has good characteristics. However, because its Mg concentration is high, there was poor cast texture quality during casting and cracks developed during hot working, for which reason there was a great decrease in yield. No. 5 had a poor electric conduction rate because it contained secondary components in excess of the range. Although No. 6 to No. 9 had the same quantities of components as the alloys of this invention, their Ni/Si or Si/Mg ratios differed. No. 6 exhibited a poor electric conduction rate because its Ni/Si ratio was high and No. 7 exhibited poor electric conductivity and solderability because its Ni/Si

ratio was low. Nos. 8 and 9 exhibited poor solderability because their Si/Mg ratios were high. No. 10 is an example in which solderability was markedly poor because the Mg content was low and the Si/Mg ratio was high. Although Comparison alloy No. 11 had the same composition as the alloys of this invention, its strength was decreased and its solderability was poor because the material temperature in the final heat treatment exceeded the upper limit of this invention. Comparison alloy No. 12, which had the same composition as the alloys of this invention, was subjected to a heat treatment in which the final heat treatment temperature was a temperature lower than the lower limit temperature of this invention. Although its mechanical properties were good, a great deal of time was required for passage of the plate through the process and solderability was poor.

[0031]

[Effect of the invention] As described above, by means of this invention, copper alloys having superior strength and electric conductivity and of superior stress relaxation characteristics and solderability were obtained, which alloys are suitable as copper alloys for electronic materials such as lead frames, terminals and connectors.

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